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URINARY EXCRETION OF S-ALKYL MERCAPTURIC ACIDS AS BIOMARKERS FOR THE EXPOSURE TO ELECTROPHILIC PRECURSORS IN TOBACCO SMOKE

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Since more than 20 years it is known that cigarette smokers excrete higher amounts of thioethers in their urine than nonsmokers. However, only a minor part of these thioethers have been identified and thus could be attributed to precursors in tobacco smoke. We determined S-methyl mercapturic acid (MMA), S-ethyl mercapturic acid (EMA), S-(3-hydroxy)propyl mercapturic acid (HPMA), S-cyanoethyl mercapturic acid (CEMA) and S-(2-hydroxy)ethyl mercapturic acid (HEMA) in urine by a newly developed method using liquid chromatography with tandem mass-spectrometry (LC-MS/MS). This method was applied to 24 h-urine samples from 68 healthy subjects (41 nonsmokers and 27 smokers). Mean urinary excretion rates (µg/24 h) in nonsmokers were 64.0 (MMA), 13.0 (EMA), 653.8 (HPMA), 1531.8 (CEMA) and 700.0 (HEMA). The corresponding values for smokers were 72.4 (MMA), 14.3 (EMA), 1624.5 (HPMA), 1797.0 (CEMA) and 529.7 (HEMA). All differences between smokers and nonsmokers except that for HPMA ($p < 0.001$) were statistically not significant. In smokers, HPMA excretion was significantly correlated to smoking dose parameters such as daily cigarette consumption ($r = 0.44$), plasma cotinine ($r = 0.53$) and urinary cotinine ($r = 0.55$). Urinary MMA and EMA excretions were also correlated to the smoking dose, however, the correlations were weaker. CEMA and HEMA excretion rates did not correlate with the smoking dose. Passive smoking as determined by questionnaire, nicotine on personal samplers and urinary cotinine was not found to be associated with the excretion of these mercaputric acids. Our results suggest that the smoking-related inhalation of acrolein giving rise to HPMA formation significantly contributes to the formation of urinary thioethers. The precursors of the other mercapturic acids in tobacco smoke are probably of minor importance for the thioether formation in smokers.

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